Pyraclostrobin and Metconazole Residues in Oilseed Rape Flowers, Nectar, and Pollen

Citation:	Barth, M. 2014. Determination of residues of BAS 556 03 F in oilseed rape inflorescences, and their respective honeybee food items. Study ID 370647. Performed by Laboratory for Biological and Chemical Analysis GmbH, Gerichshain, Germany. Sponsored by BASF SE, Ludwigshafen, Germany.
Chemicals	Pyraclostrobin and Metconazole
PC Codes:	099100, 125619
CAS #:	175013-18-0, 125116-23-6
MRID:	49459605
EPA Guideline:	Non-guideline
GLP Statement:	This study was conducted in compliance with OECD Principles of Good Laboratory Practice (1997)
Classification:	The study is classified as "**Supplemental**" and may be used quantitatively in risk assessments.
Date of Study Completion:	July 17, 2014

EPA Primary Reviewer:	Meghan Radtke, Ph.D., Biologist	Signature: Date: 4/10/15	
EPA Secondary Reviewer:	Ryan Mroz, Biologist	Signature: Date: 4/16/15	

Summary
The objective of this study was to determine residues in winter oilseed rape (*Brassica napus* L.) pollen, nectar, and whole flowers after being treated with one application of BAS 556 03 F (13% pyraclostrobin and 8% metconazole product).

In 2013, five separate locations in Europe were chosen for the study: Eastern Germany (trial 1), Southern Germany (trials 2 and 3), Western Germany (trial 4), and Poland (trial 5). Each location had one untreated control field and a nearby field treated with BAS 556 03 F at an application rate of 1.27 lb pyraclostrobin/A and 0.71 lb metconazole/A. Fields ranged from 0.54 to 1.33 ha in size. Foliar spray applications were made to flowering oilseed rape fields on May 5th (trial 1), May 9th (trials 2 and 3), May 8th (trial 4), and May 20th (trial 5) in 2013. No other pyraclostrobin or metconazole applications were made during the experiment or the previous year (2012); however the oilseed rape seeds received seed treatments of Elado (trials 1-4), Thiram (trial 1), and Cruiser (trial 5). These are not expected to have affected pyraclostrobin and metconazole residue levels within the plants.

Residue samples were collected from each plot at two time periods: within 24 hours of application and 7 days after the application. Pollen (2 g) and flowers (10 g) were collected directly from the rapeseed plants. Pollen was collected from full flowering inflorescences by transferring the anthers/stamina into a specimen container. Nectar (2 g) was extracted using a capillary tube from cut rapeseed flowers in the field. Samples were collected from across the entire plot and were pooled together for the analysis.

Samples were deep frozen by placing on dry ice immediately after collection and then stored at the test facility at ≤ -18°C. Samples were shipped deep frozen to the analytical lab (SGS Institut Fresenius GmbH) on June 6, 2013.

BASF method L0076/01, which determines the concentration of BAS 556 03 F by LC-MS/MS, was used to measure residues in the samples. The LOQ was 0.01 mg/kg and the LOD was 0.001 mg/kg for both metconazole and pyraclostrobin. Samples were analyzed between October 9 and 11, 2013. Percent recoveries from known spiked samples are reported in Table 1.

Table 1. Recoveries of pyraclostrobin and metconazole. The lowest fortification level is at the LOQ.

Substrate	Fortification Level	Pyraclostrobin (%)	Metconazole (%)
Pollen	0.01 mg/kg	75.3	82.8
	0.1 mg/kg	78.4	79.2
Nectar	0.01 mg/kg	73.0	79.4
	0.1 mg/kg	75.1	79.9
Flowers	0.01 mg/kg	86.9	92.2
	0.1 mg/kg	87.8	91.6

Pyraclostrobin and metconazole residues were not detected in any of the control samples, and are thus not reported in Table 2. The highest residues were detected in flowers, with a maximum of

nearly 21 mg/kg. All residues decreased in magnitude from the initial measurement on the day of application to the second sample taken 7 days later (Table 2).

Table 2. Range of pyraclostrobin and metconazole residues from treated fields

	Day After Application	Pyraclostrobin (mg/kg)	Metconazole (mg/kg)
Nectar	0	0.057 to 0.231	0.062 to 0.305
	7	<0.001 to 0.023	0.004 to 0.033
Pollen	0	1.075 to 7.787	0.631 to 4.582
	7	0.010 to 0.222	0.009 to 0.102
Flowers	0	8.557 to 20.994	4.823 to 21.314
	7	0.361 to 2.915	0.363 to 1.974

Study Limitations

The residue samples were not analysed immediately, but were stored for approximately 5 months at ≤ -18° C. The report indicates that pyraclostrobin and metconazole are stable for 2 months. Since there were no matrix spike samples associated with the sample during sample collection and storage, the residue stability for 5 months is uncertain. Therefore, the study may underestimate the pyraclostrobin and metconazole residue levels because of potential degradation during the sample storage. In addition, it is uncertain if the analytical method was validated by an independent laboratory.

References

BASF Method Number L0076/01 (535/1): Method for the determination of alphacypermethrin and cypermethrin in plant matrices, 01 Feb 2005.